NASA ASTROBIOLOGY INSTITUTE ANNUAL REPORT YEAR 4

[July 2001 – June 2002]

Project Report: Delivery of Organic Materials to Planets

Harvard University
Executive Summary
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The study of the ways in which Earth's first environments originated and evolved is, to a large extent, a study of the history of oxygen. The planet's most abundant element, oxygen occurs in Earth's crust, in its freshwater, in its seawater, and in its atmosphere; it is of quintessential importance to virtually all life. Practically all Earth's free oxygen was formed as a result of photosynthetic processes carried out by cyanobacteria and the early plants, processes through which organic compounds are synthesized from carbon dioxide and water in the presence of sunlight.

The Harvard NAI team was constituted in 1998 as an interactive group of biogeochemists, paleontologists, sedimentary geologists, geochemists, and tectonic geologists assembled with the common goal of understanding the coevolution of life and environments in Earth history. The team originally proposed to focus multidisciplinary research on four critical intervals of planetary change: (1) the early Archean (>3,000 million years ago, or Ma) when life began, (2) the early Paleoproterozoic (2,400−2,200 Ma) when oxygen began to accumulate in the atmosphere and surface ocean, (3) the terminal Proterozoic and Early Cambrian (750−525 Ma) when animal life radiated, and (4) the Permo−Triassic boundary (251 Ma) when mass extinction removed some 90 percent of Earth's species diversity, permanently altering the course of evolution. Given reduced funding levels in Years 1 and 2, however, the team chose to focus on the latter three intervals, and team members have made substantial contributions to each research area. On the other hand, increased funding in Years 3 and 4 and strong interest by colleagues at Harvard and the Massachusetts Institute of Technology (MIT) have enabled us to expand both our membership and intellectual purview. Thus, to the three projects funded from the outset (and approached in fresh ways by our newest co−investigators), we have expanded research at the interface of microbiology and biogeochemistry; bolstered the team's collaborative research in biogeochemisty; and undertaken research on Neogene iron formations in Spain in order to help guide rover research on the Mars hematites during the 2003 Mars Exploration Rover (MER) mission. Work continues on the statistical analyses of molecular sequence and biostratigraphic data as part of the NAI Focus Group on Evogenomics.

Scope of Team Activities in 2001−2002

Research by the Harvard team is interdisciplinary, attracting increasing participation by scientists within the five member institutions (Harvard University, MIT, Woods Hole Oceanographic Institute (WHOI), Rochester Institute of Technology, and the Smithsonian Institution). We have also been successful in promoting cross−team collaborations −− currently, research projects are under way with colleagues from the Carnegie Institute of Washington (CIW), MBL, the University of Rhode Island, Pennsylvania State University, NASA Ames Research Center, and the Jet Propulsion Laboratory (JPL) teams, as well as both the Spanish and Australian astrobiology centers. Moreover, our team participates actively in the Evogenomics Focus Group and has taken a leadership position in the Mission to Early Earth Focus Group. Team members are active in research on novel biosignatures and digital mapping technologies that can be applied to Solar System research, and are members of the 2003 Mars MER science team and serve on MEPAG (Mars Exploration Payload Assessment Group) and the Astrobiology Science Strategy Group, committees charged with defining astrobiological research strategies for upcoming Mars missions. Equally important, research by Harvard team members on sedimentary and geochemical biosignatures, as well as early states of Earth's atmosphere, directly influence planning for continuing planetary exploration and the projected Terrestrial Planet Finder (TPF) mission.

The Harvard team has a particularly active field presence, with projects currently under way in Australia, southern Africa, Svalbard, Canada (Newfoundland and the Rocky Mountains), China, Oman, and Spain. We also teach at three universities, contributing to both the training of new professionals and the education of a broader university community. Basic courses in geobiology and Earth systems science are offered at MIT, Harvard, and Rochester. During the past year, an advanced geobiology/astrobiology course was initiated at MIT, and, at Harvard, a graduate seminar on biomineralization was presented. This year, much of our EPO effort was focused on university teaching, but individual team members also lectured to K−12 and adult groups (including space engineers at JPL), we sponsored a public lecture and organized a Pardee Keynote Symposium on geobiology and astrobiology for the 2001 annual meeting of the Geological Society of America.

Research Accomplishments in 2001−2002

Subproject 1: The Proterozoic Oxidation of the Earth's Surface

The history of oxygen in the oceans and atmospheres is thought to have played a key role in Earth's long−term biological evolution. Ongoing research by Harvard team members addresses the initial oxygenation of the atmosphere and surface ocean 2,400−2,200 million years ago (Ma), renewed oxygen influx near the end of the Proterozoic eon, and life and environments between those two events.

In 1998, it was proposed that the cessation of iron formation deposition ca. 1850 Ma reflected the expansion of sulfidic deep oceans and not, as traditionally understood, the spread of oxygen throughout ocean basins. Research by Harvard team members lends support to this hypothesis, demonstrating the presence of a strong redoxcline within the ca.1,500−Ma

Roper group, Australia, and documenting an environment−specific pattern of sulfur isotopic fractionation that documents low sulfate levels in Roper seawater. Roper and older sedimentary rocks in northern Australia suggest sulfate (and, hence, probably oxygen) limitation through 250 million years of mid−Proterozoic history. One wishes, however, for geochemical markers that might provide globally integrated records of Proterozoic redox conditions. It was shown that molybdenum (Mo) isotopes may serve this purpose. Systematic differences were observed between the Mo isotopic compositions of sediments accumulated under oxic and sulfidic conditions. Preliminary data led to the prediction that Mo isotopes are fractionated during uptake by manganese (Mn) oxides. Laboratory experiments conducted in the fall of 2001 confirm this hypothesis. The measurements of sulfidic sediments beyond the Black Sea, characterizing Mo isotopes in Cariaco Basin sediments, have been extended. Molybdenum isotopes here are very similar to those of the Black Sea. Finally, as this year drew to a close, made preliminary measurements were made of Mo isotopes in mid−Proterozoic black shales, measurements that are consistent with the hypothesis of extensive ocean anoxia at this time; also, the implications of sulfidic deep waters for the distribution of biologically important trace metals in Proterozoic oceans have been explored.

The factors that led to the formation of sulfidic Proterozoic oceans remain uncertain, as do the processes that facilitated renewed oxygen increase toward the end of the eon. In modeling the initial rise of atmospheric oxygen levels 2,400−2,200 Ma, it is proposed that a minor increase in the oxygen fugacity of volcanic gases may have triggered the Paleoproterozoic rise of atmospheric oxygen.

Subproject 2: Neoproterozoic−Cambrian environmental change and evolution

This subproject has enjoyed the broadest participation of Harvard team members, and for good reason. The Proterozoic−Cambrian transition witnessed remarkable changes in tectonics, climate, atmospheric composition, and, especially, life. This is the interval during which animal life −− and, hence, the prospect of intelligence −− radiated on Earth. Harvard team researchers are studying the paleontology, geochronology, tectonics, and environmental changes of this interval, with an eye to constructing models of integrated change in the Earth system.

During the past year, thin volcanic ash beds below, within, and above the Gaskiers glacial deposits in Newfoundland were dated; ashes in the region from 8 meters below the glacial deposits to 10 meters above have ages within error of one another and cluster near 580 Ma. These are the first high−precision temporal constraints on the age and duration of a Neoproterozoic glaciation. The oldest known Ediacaran fossils lie approximately 100−200 meters above the glacials and are 575 Ma, leaving approximately 5 Ma between the last glacial deposit and the initial expansion of large animals.

The dramatic diversification of animal phyla during early Cambrian time has fueled debate regarding the mechanisms of early animal evolution for over a century. What is now clear is that intrinsic catalysts, such as the innovation of developmental genetic mechanisms, as well as extrinsic processes, involving environmental change, are both critically important in accounting for this major event in the history of life. Recent attempts to define potential extrinsic factors have revealed a large−magnitude, but short−lived negative excursion in the carbon−isotopic of seawater that is globally coincident with the Precambrian−Cambrian boundary. Possible mass extinction, in some manner related to this negative isotope excursion, has been invoked as a contributing mechanism that led to rapid diversification of metazoans within restructured early Cambrian ecosystems. Research on biostratigraphic, geochemical, and geochronometric data from Oman supports this hypothesis, indicating an extinction of terminal Proterozoic calcified metazoans coincident with this boundary isotope excursion ca. 542 Ma.

Exploration of the theory, phenomenology, and consequences of Snowball glaciation on the late Proterozoic Earth continues. Field programs focus on the geology and isotopic records of carbonate successions in Namibia, Svalbard, Morocco, and Canada, that together span the critical time interval from around 850 to 530 Ma (mid−Neoproterozoic through the Cambrian “explosion”). This interval includes three glacial episodes with unusual features that form the basis for the “Snowball earth” hypothesis. Three new tests of the hypothesis are under way: (1) a geochemical search for interplanetary dust (which predictably should have accumulated on the global ice shell) targeted at a newly discovered clay layer that separates the glacial deposits from postglacial cap carbonate; (2) a study of boron isotopes before and after glaciation, when seawater pH is predicted to have been abnormally high (alkaline) and low (acidic), respectively: and (3) an oxygen, sulfur, and strontium isotopic study of primary barite seafloor cements discovered in postglacial cap carbonates. This research is complemented by geochemical analyses and modeling efforts. Of particular interest, the presence of a large negative carbon isotope anomaly just before the glaciation, suggests that methane may play a role in the Snowball Earth phenomena. A novel hypothesis is proposed in which the release of methane from sediments may actually cause the glaciation through its interaction with silicate weathering.

Subproject 3: Permo−Triassic mass extinction and its consequences

At 251 Ma, more than 90% of marine species disappeared; land ecosystems were similarly devastated. Harvard team members seek to understand the causes and evolutionary consequences of this greatest of all mass extinctions. During the past year, field and laboratory research has continued on the timing of the Permian−Triassic (P−Tr) mass extinction, focusing on the earliest pulse of extinction and seeking to learn, through field study and radiometric dating of ash samples, whether land and sea extinction occurred synchronously. Modeling of end−Permian oceanographic conditions continues, helping to constrain scenarios for the largest known mass extinction. It has been shown that if ocean circulation were weaker than it is now, consumption of oxygen could outstrip oxygen supply to the deep oceans, leading to anoxic deep waters rich in dissolved carbon. Were a rapid change in circulation to flush such a deep ocean, the rapid release of carbon dioxide to the atmosphere could have a significant effect on biology, perhaps triggering extinctions. Continuing research focuses on geological tests of model results, including expected carbon isotopic signatures.

Exploration of microchemical techniques that illuminate the physiology of fossilized organisms is ongoing. It has been demonstrated that x−ray microspectroscopy allows detection of lignin−derived aromatic compounds in ancient tracheids and that the conducting cells of early land plants were not lignified. Such microchemical techniques will be important when it comes time to analyze small samples returned from Mars.

Subproject 4: Molecular and isotopic approaches to microbial ecology and Biogeochemistry

Astrobiology research continues to focus on novel applications of isotopic biogeochemistry. Research on the C−isotopic measurement of SSU (small subunit) ribosomal RNA (or rRNA) genes has borne its initial fruit, providing a technique that can provide both phylogenetic and physiological information on organisms present in natural ecosystems. Collaboration in measuring bacterial fractionations of hydrogen isotopes (with the NASA Ames Astrobiology team) led to an extensive paper describing the sources of hydrogen (H) used in biosynthesis of lipids by the aerobic methanotroph, *Methylococcus capsulatus,* and the isotopic fractionations associated with its biosynthetic pathways. H−isotopic analyses of an extensive series of oils from Australia have been completed. The results suggest that hydrogen isotopic compositions of sedimentary hydrocarbons are minimally affected by diagenetic processes and so can be used to resolve mixtures of sedimentary compounds with distinct biological sources.

Research is conducted on the chemical and isotopic characterization and biogeochemical significance of lipids from cultured microbes, environmental samples, and their fossil analogues in ancient sedimentary environments. Currently, the lipids of a number of new isolates of thermophilic and hyperthermophilic bacteria are being analyzed, greatly extending our understanding of the variety and complexity of extremophile lipid biosignatures. Preliminary research has begun on organic−rich, low−maturity sediments that span both the Precambrian−Cambrian (Oman) and Permo−Triassic (Australia) boundaries, with the goal of detecting molecular biomarkers that might be diagnostic for biogeochemical processes.

Subproject 5: Geobiology of Neogene hematitic sedimentary rocks

In 2003, NASA will launch two lander missions to Mars. One of the landers is slated to touch down in a region marked by aqueous hematite deposition. If we are to maximize the scientific opportunities of this mission, we must first complete careful studies of analogous systems on Earth, where biological and physical processes can be tied directly to paleobiological and geochemical patterns in deposited iron−rich sediments. The Rio Tinto drainage area of southern Spain offers just such an opportunity. During this year, we completed two field sessions in the Rio Tinto region with colleagues from the Spanish CAB. Using a combination of petrology, Moessbauer spctroscopy, and x−ray diffraction (XRD), we established that iron−sediments precipitated from Rio Tinto waters are primarily hydronium jarosite, with unusual Fe−sulfates (iron sulfates) such as copiapite and poorly ordered iron oxides forming late in the season, when water pools evaporate to dryness. Early in diagenesis, highly soluble jarosites are replaced by goethite, which has a high capacity for preserving cellular details of cells and tissues caught up in Rio Tinto sediments. In ca. 300,000−year−old terraces, much goethite has, in turn, been replaced by hematite, some of which is coarse grained. Thus, through diagenesis, Rio Tinto sediments come to resemble hematites observed on the Martian surface. Comparison of modern and Pleistocene sediments also shows that aspects of physical and biological environments are encrypted in the textures of Fe−sediments, providing a basis for the interpretation of images returned from the Mars MER rover.

Subproject 6: Evogenomics (Collaborative focus group research)

This year research was conducted to improve confidence intervals in paleontological estimates of the evolutionary first and last appearances of taxa and on reconciling molecular clock and paleontological estimates of evolutionary divergence times. Research has also continued on the construction of a global database for the fossil record that will enable paleontologists to understand the history of biological diversity and facilitate the differentiation of the biological from geological signals in Phanerozoic marine diversity studies. In an important development, it was shown that the algorithm from which it was inferred that marine diversity has not increased since the Paleozoic fails to take beta−diversity into account.

Figures

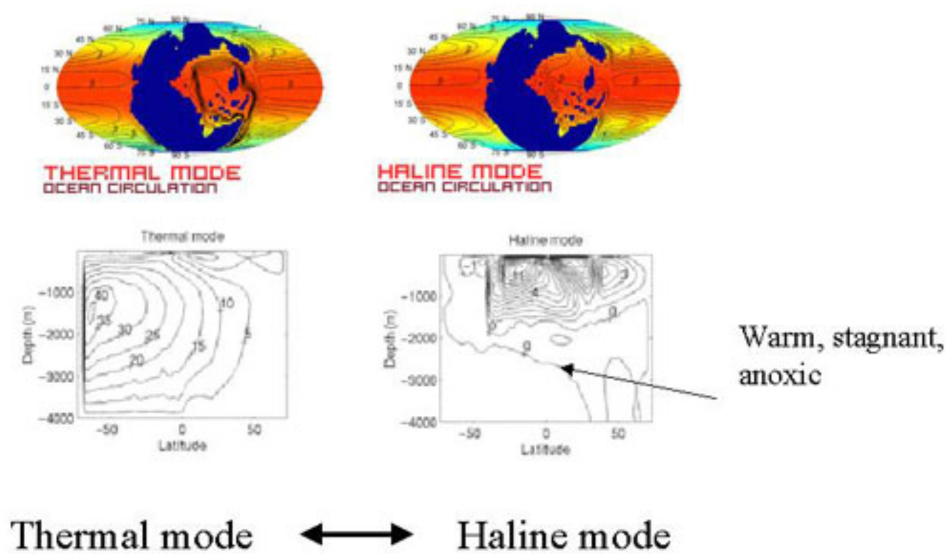

Figure 1. Schematic depiction of how changing ocean redox conditions through time influenced the depth distributions of the biologically important trace metals Mo (dashed lines) and Fe (solid lines). In the Archean ocean, O_2 (green) is presumed to be scarce, although locally high levels might have been possible in association with cyanobacterial blooms. The deep ocean concentration of Mo is much lower than that of Fe. In the mid−Proterozoic ocean (1,850 − 1,250 Ma), moderate concentrations of oxygen are found in

surface waters, but deep waters are sulfidic (black). Overall concentrations of both metals are depressed by removal in sulfidic deep waters; depth profiles are similar to those in the modern Black Sea. In the Phanerozoic (<543 Ma) ocean, oxygen occurs throughout the water column. In consequence, Fe is scarce, and Mo is moderately enriched.

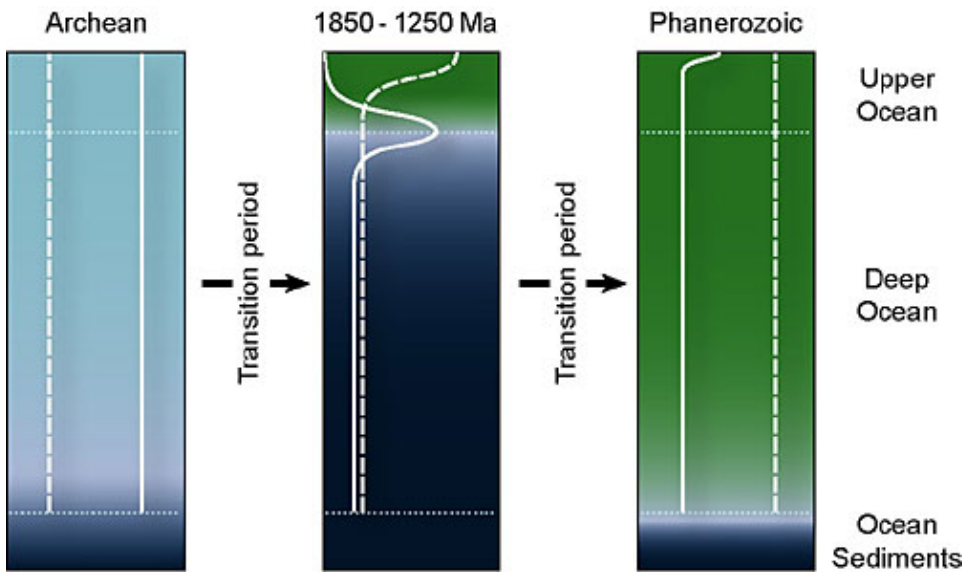

Figure 2. Coupled physical oceanographic and biogeochemical models suggest that late Permian oceans might have varied from thermally driven circulation, with oxygenated deep waters, and haline circulation with much expanded deep−water anoxia. Understanding late Permian environments is key to evaluating hypotheses for the great end−Permian mass extinction.

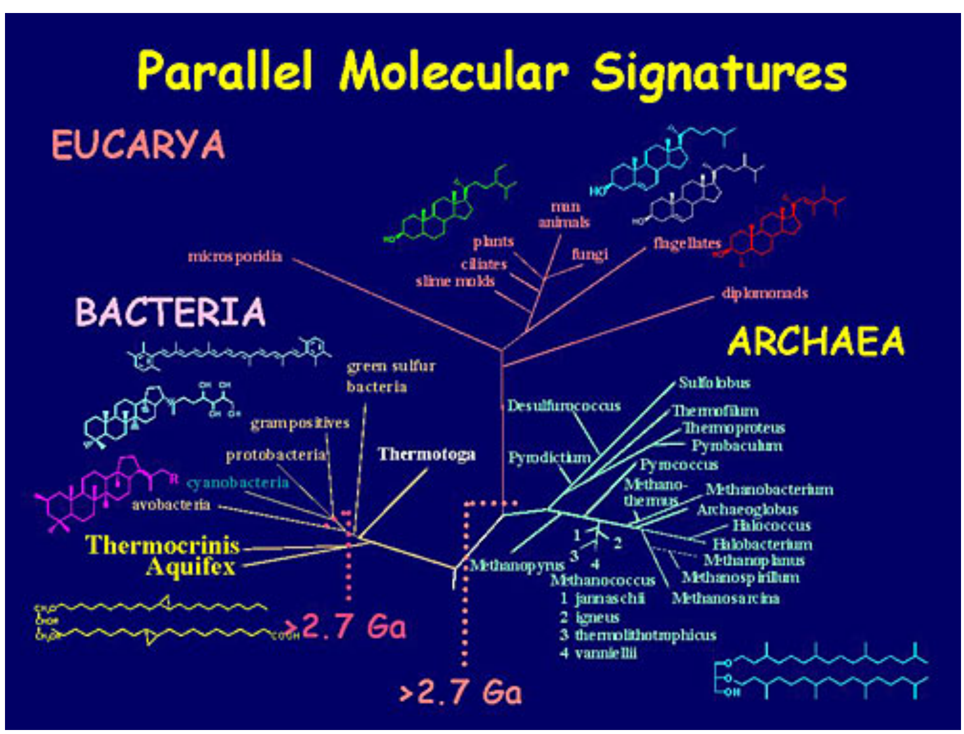

Figure 3. The Tree of Life, a depiction of the genealogical relationship of all organisms, based on molecular sequence comparison, with diagnostic lipid molecules shown for each domain. Molecular biomarkers play an important role in studies of ancient life and environments on Earth and provide a promising set of biosignatures for astrobiological exploration.